KINETIC AND SIMULATION STUDIES OF THE ESTERIFICATION OF ACRYLIC ACID WITH 2-ETHYL HEXANOL IN A BATCH AND PACKED BED REACTOR

MOHD AMIRUL ASYRAF BIN AHMAD

Doctor of Philosophy

UNIVERSITI MALAYSIA PAHANG

SUPERVISOR'S DECLARATION

We hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Doctor of Philosophy

____

(Supervisor's Signature)

Full Name : DR CHIN SIM YEE

Position : ASSOCIATE PROFESSOR

Date :

____

(Co-supervisor's Signature)

Full Name : DR SUMAIYA BT ZAINAL ABIDIN @ MURAD

Position : ASSOCIATE PROFESSOR

Date :

STUDENT'S DECLARATION

I hereby declare that the work in this thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at Universiti Malaysia Pahang or any other institutions.

____

(Student's Signature)

Full Name : MOHD AMIRUL ASYRAF BIN AHMAD

ID Number : PKC15006

Date :

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MOHD AMIRUL ASYRAF BIN AHMAD

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ABSTRAK

Air sisa yang mengandungi asid akrilik (AA) menjejaskan alam sekitar disebabkan oleh keperluan oksigen kimia yang tinggi. Pemulihan AA daripada air sisa secara esterifikasi dalam reaktor berpenyuling mungkin berbaloi. Kebiasanya, kajian kebolehlaksanaan proses perolahan ini dijalankan dalam proses batch bagi menentukan tindak balas kinetik. Hal ini tidak mencukupi untuk menentukan data asas penting lain seperti pemindahan jisim dan pencampuran yang juga sangat diperlukan semasa reka bentuk reaktor. Pertimbangan ini penting untuk melihat prestasi dan masalah seperti pembasahan pemangkin yang tidak lengkap, rintangan pemindahan jisim yang tidak baik, atau ketidakseratataan taburan. Dalam kajian ini, kajian tentang pemangkin resin penukar ion heterogenous dan penyesuaian tetingkap operasi untuk tindakbalas pengesteran untuk memulihara AA dari sisa kumbahan dilaksanakan. Data asas seperti kinetik tindak balas, pemindahan jisim dan pencampuran untuk simulasi, reka bentuk dan pembinaan proses perolahan seperti reactor berpenyuling dan reaktor kromatografi untuk memulihara AA dari sisa kumbahan juga diperoleh. Reaktor pemangkin padat beraliran berterusan, sistem yang menyerupai bahagian reaktor dalam reaktor berpenyuling digunakan untuk pengesteran AA dengan 2-etil hexanol (2EH). Pemangkin resin kation yang mempunyai fungsi kimia asid sulfonik yang terbaik, SK104, SK1B, PK208, PK216, PK228, RCP145, dan RCP160, telah disaring dalam sistem batch. PK208 mendahului resin lain dan ia kemudiannya dipilih untuk digunakan dalam kajian seterusnya. Eley-Rideal (ER) merupakan model kinetik terbaik untuk mengaitkan kadar penghasilan 2EHA. Pengesterifikasian endoterma AA dengan 2EH ditunjukkan oleh peningkatan pemalar keseimbangan dengan suhu. Kesan parameter penting seperti kepekatan awal AA, suhu, nisbah molar bahan tindak balas (AA:2EH), kuantiti pemangkin, dan kuantiti penghalang pempolimeran telah dikaji dengan menggunakan reka bentuk 2 faktorial untuk melihat kesan pengaruh proses esterifikasi. Kepekatan awal AA dan suhu mempengaruhi proses esterifikasi AA dengan 2EH yang tertinggi. Memandangkan pengaruh kuantiti penghalang pempolimeran tidak ketara, faktor ini telah digugurkan untuk kajian seterusnya. Kuantiti penghalang pempolimeran yang terdapat dalam AA mentah mencukupi untuk menghalang pempolimeran AA. Taburan masa mastautin dikaji untuk memeriksa kelakuan pencampuran dalam sistem. Disebabkan masalah penyaluran yang teruk berlaku, sangkar pemangkin dipasang. Kajian penjerapan menggunakan campuran dedua tidak reaktif dilakukan untuk melihat keafinan resin terhadap setiap sebatian. Keafinan resin PK208 terhadap sebatian yang terlibat dalam sintesis 2EHA dalam tertib menurun ialah: air>AA>2EH/2EHA. Prestasi pemangkin resin PK208 untuk pengesteran antara AA dan 2EH kemudian dinilai dalam reaktor pemangkin padat (RPP) pada pelbagai suhu (55-90ºC), kuantiti pemangkin (1-15 g), nisbah molar (1:1-1:5), dan kadar aliran suapan (1-5 ml/min). Keadaan terbaik yang memberikan penukaran tertinggi ialah 66.44mol% pada 95ºC, dengan kuantiti pemangkin 5g, nisbah molar AA: 2EH 1: 3, dan aliran suapan 1 ml/min. Dibandingkan dengan sistem batch, pengaruh kepekatan awal AA tidak lagi ketara. Simulasi RPP yang dilakukan menggunakan model reaktor aliran palam menunjukkan hasil yang diramalkan tersasar sedikit dari data eksperimen, kerana berlakunya penyerakan dalam RPP seperti yang terbukti dengan kajian taburan masa mastautin. Data eksperimen RPP berpadanan dengan hasil simulasi yang dijana daripada model reaktor pemangkin padat yang mengambil kira penyerakan paksi di RPP. Justeru, tetingkap operasi yang dikenal pasti dan data asas telah membuktikan potensi RDC dalam menukar AA dalam air sisa dengan kecekapan yang lebih baik.

ABSTRACT

Wastewater containing acrylic acid (AA) imposes detrimental effect to the environment due to its high value of chemical oxygen demand. Recovery of AA from its dilute aqueous solution for heterogeneously catalysed esterification in a reactive distillation column (RDC) could be a promising approach. Typically, the feasibility study of these intensified processes was carried out in batch process to determine the reaction kinetics. It is insufficient to determine the other important fundamental data such as mass transfer and mixing which are also crucially required during the equipment design. This consideration is important to observe the probability of underperformance due to the problems such as incomplete catalyst wetting, severe mass-transfer resistances, or maldistribution. In the present study, the investigation on the suitable heterogeneous IER catalyst and appropriate operating window for the esterification reaction to recover AA from the wastewater was conducted. The fundamental data includes reaction kinetics, mass transfer and mixing for simulate, design, and construction of the intensified RDC and CR for the recovery of AA from the wastewater would also be obtained. The continuous flow tubular packed bed reactor (PBR), a system mimicking the reactive section in the intensified processes was used. The best sulfonic acid functional cation-exchange resin catalysts, SK104, SK1B, PK208, PK216, PK228, RCP145, and RCP160, were screened in a batch system. PK208 outperformed the other resins and it was used in subsequent studies. Eley-Rideal (ER) was the best kinetic model to correlate the production rate of 2EHA. Endothermicity of the AA esterification with 2EH was indicated by the increase of its equilibrium constant with temperature. The critical factor that contribute toward reaction performance include initial concentration of acrylic acid (AA), temperature, molar ratio of reactant (AA and 2EH), catalyst loading, and polymerisation inhibitor loading was studied using 2 factorial designs. Initial concentration of AA and temperature was found affected the esterification of AA with 2EH the most. Since the contribution of additional polymerisation inhibitor loading was not significant, this factor has been neglected to be studied in further experiment. The existing amount of the polymerisation inhibitor contained in raw AA is sufficient to avoid AA polymerisation. Residence time distribution (RTD) was studies to examine the mixing behavioural of system. Due to the severe channelling occurred, catalyst cage need to be install. An adsorption study using nonreactive binary mixtures was performed to observe the affinity of resin against each compound. The affinity of PK208 resin towards the chemical species involved in 2EHA synthesis in descending order is: water> AA> 2EH/2EHA. Catalytic performance of resin PK208 for the esterification between acrylic acid (AA) and 2-ethyl hexanol (2EH) was then evaluated in packed bed reactor (PBR) under various temperatures (55-90ºC), catalyst loadings (1-15 g), molar ratios of AA to 2EH (1:1-1:5), and feed flow rates (1-5 ml/min). The best condition that gave highest yield, 66.44mol% was at 95 ºC, with catalyst loading of 5 g, molar ratio AA:2EH of 1:3, and feed flow of 1 ml/min. In contrast to the batch system, the effect of initial concentration of AA was found to be not significant anymore. The PBR simulation performed using plug flow reactor model showed that the predicted results deviated marginally from the experimental data, owing to the occurrence of dispersion in PBR as proven by the residence time distribution (RTD) study. The PBR experimental data well matched with the simulation results generated from the packed bed reactor model considering the axial dispersion in PBR. Thus, the identified operating window and fundamental data validated the potential of RDC in converting the AA in wastewater with the better efficiency.

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LIST OF SYMBOLS

%	Percent
C_M	Mears parameter
$r_{A,obs}$	Observed reaction rate
R_C	Catalyst particle radius
ρ_b	Bulk density of catalyst
C_{Ab}	Bulk concentration
k_C	Mass transfer coefficient
D_{AB}	Diffusivity of the solute A in solution
d_p	Diameter of the catalyst particle
μ_C	Viscosity of the solution
G	Gravitational acceleration
ρ_l	Density of the solution
C_{WP}	Weisz-Prater parameter
D_{eff}	Effective diffusivity
ΔG^{o}	Gibbs energy
ΔH_r^{o}	Free enthalpy of reaction
ΔH_{rxn}	Heat of reaction
Å	Armstrong
A_{cs}	Adsorbate cross sectional area
a_i	Activity coefficient of component i
b_i	i^{th} adjustable variable
C_i	Concentration of component
d_p	Particle diameter
E_f	Activity energy of reaction
K_a	Thermodynamic equilibrium constant
K_{eq}	Equilibrium constant
k_f	Rate constant
k_{f0}	Pre-exponential factor
K_i	Adsorption equilibrium constant for species i
K_x	Apparent equilibrium constant

M	Molecular weight of adsorbate
N	Number of experimental points
N_{Av}	Avogadro's number
P/P°	Relative pressure
R	Gas constant
R^2	Coefficient of determination
r_i	Rate of reaction of component
T	Reaction temperature
t	Reaction time
w	Catalyst weight
W_m	Weight of adsorbate
X_e	Degree of equilibrium conversion
x_i	Mole fraction of component i
γ_i	Gamma of component i
σ	Standard deviation

LIST OF ABBREVIATIONS

2EH	2 ethyl hexanol
2EHA	2 ethyl hexyl acrylate
AA	Acrylic acid
BET	Brunauer, Emmett and Teller
BJH	Barrett-Joyner-Halenda
COD	Chemical oxygen demand
EQA	Environment Quality Act
ER	Eley Rideal
FID	Flame ionization detector
FTIR	Fourier transform infrared
GC	Gas chromatography
IUPAC	International Union of Pure and Applied Chemistry
LHHW	Langmuir-Hinshelwood-Hougen-Watson
PH	Pseudo homogeneous
PVC	Poly(vinyl chloride)
RDC	Reactive distillation column
SMBR	Simulated-moving-bed reactor
TOC	Total organic carbon
UNIFAC	Universal functional activity coefficient
W	Water

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